Effect of the spin-orbit interaction and the electron phonon coupling on the electronic state in a silicon vacancy

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Abstract. The electronic state around a single vacancy in silicon crystal is investigated by using the Green's function approach. The triply degenerate charge states are found to be widely extended and account for extremely large elastic softening at low temperature as observed in recent ultrasonic experiments. When we include the LS coupling $\lambda_{\rm Si}$ on each Si atom, the 6-fold spin-orbital degeneracy for the V^+ state with the valence +1 and spin 1/2 splits into Γ_7 doublet groundstates and Γ_8 quartet excited states with a reduced excited energy of $O(\lambda_{\rm Si}/10)$. We also consider the effect of couplings between electrons and Jahn-Teller phonons in the dangling bonds within the second order perturbation and find that the groundstate becomes Γ_8 quartet which is responsible for the magnetic-field suppression of the softening in B-doped silicon.

1. Introduction

Recently, Goto *et al.* have succeeded in the direct observation of the isolated vacancy in high-purity crystalline silicon (Si), with extremely low vacancy concentration believed less than 10^{15} cm^{-3}, through the ultrasonic measurements at low temperature[1, 2]. They have measured the elastic constants of two type samples, non-doped Si, and boron (B)-doped Si and observed reciprocal temperature dependence below 20 K down to 20 mK, called 'elastic softening', without the sign of the local distortion[1]. The softening of non-doped Si is independent of the external magnetic fields up to 10 T, while that of boron (B)-doped Si is suppressed by the external magnetic fields of the order of 1 T. They have claimed that (1) the softenings are cause by the isolated vacancy groundstates with 3-fold orbital degeneracy coupled to the ultrasound and (2) non-doped Si has the non-magnetic neutral charge state V^0 and B-doped Si has the charge state V^+ with the valence +1 and the spin 1/2[1]. Based on the standard theory of vacancy[3, 4, 5] established in 1980's, the groundstate degeneracies for both V^0 and V^+ states are resolved with symmetry lowering due to the Jahn-Teller distortion in contrast to the newly observed softening.

To understand such anomalous softenings, new approaches focusing on the quantum many-body effect have been performed on the basis of cluster model for the dangling-bond orbitals in a Si vacancy in a couple of years[6, 7, 8]. Yamakawa *et al.*[6, 7] have revealed that the effect of couplings between electrons and Jahn-Teller phonons as well as that of Coulomb interaction in the dangling bonds play crucial roles for the electronic states of both V^+ and V^0 states. Matsuura and Miyake[8] have studied the effects of spin-orbit interaction and the Coulomb interaction, and have found that the Γ_8 quartet groundstate, which is responsible for the magnetic suppression

of the softening in B-doped Si, is realized in the V^+ state by assuming a negative value of the spin-orbit coupling on the vacancy state $\lambda_{\rm vc} < 0$, although the explicit calculation for $\lambda_{\rm vc}$ has not been done so far.

In the cluster model calculations mentioned above, the effect of the spatial extension of the vacancy state, which is important to determine the absolute value of the elastic softening, has not been considered. In our previous paper[9], we have investigated the electronic state around a single vacancy in infinite Si crystal on the basis of the Green's function approach, and found that the T_2 triplet vacancy states are widely extended up to 20 Å and are responsible for the extreme enhancement of the Curie constant of the quadrupole susceptibilities resulting in the elastic softening at low temperature. The Curie constant for the trigonal mode is considerably larger than that for the tetragonal mode as observed in the ultrasonic experiments[1]. The effect of the spin-orbit interaction, however, has not been considered there.

The purpose of this paper is to elucidate the effect of the spin-orbit interaction on the widely extended vacancy states. For this purpose, we extend our previous study[9] for the case with the LS coupling $\lambda_{\rm Si}$ on each Si atom, and then we calculate the spin-orbit splitting in the vacancy state $\Delta_{\rm vc}$ by using the Green's function approach. We also consider the effect of couplings between electrons and Jahn-Teller phonons in the dangling bonds within the second order perturbation.

2. Model and Formulation

Our model Hamiltonian consists of the tight-binding (tb) Hamiltonian $H_{\rm tb}$ with LS-coupling on each Si site and a vacancy potential $H_{\rm vc}$, and explicitly given by

$$H = H_{\rm tb} + H_{\rm vc}, \tag{1}$$

$$H_{\rm tb} = \sum_{ij}\sum_{mm'}\sum_{\sigma} t_{ij}^{mm'} c_{im\sigma}^{\dagger} c_{jm'\sigma} + \sum_{i}\sum_{mm'}\sum_{\sigma\sigma'} \lambda_{\rm Si} M_{mm'}^{\sigma\sigma'} c_{im\sigma}^{\dagger} c_{im'\sigma'} = \sum_{\mathbf{k}}\sum_{\rm s=1}^{16} \epsilon_{\mathbf{k}s} c_{\mathbf{k}s}^{\dagger} c_{\mathbf{k}s}, \tag{2}$$

$$H_{\rm vc} = \Delta \sum_{m\sigma} c_{0m\sigma}^{\dagger} c_{0m\sigma}, \tag{3}$$

where $c_{im\sigma}^{\dagger}$ is a creation operator for an electron at site i and orbital m $(= 3s, 3p_x, 3p_y, 3p_z)$ with spin σ, and $c_{\mathbf{k}s}^{\dagger}$ is that for wave vector $\mathbf{k}$ and band s $(= 1 \sim 16)$. In first term of eq. (2), the tb parameters $t_{ij}^{mm'}$ are written by the Slater-Koster parameters and determined so as to fit the tb band energies $\epsilon_{\mathbf{k}s}$ to the LDA band energies[12] for the Si crystal, and explicitly given in Ref [9]. The second term in eq. (2) represents LS-coupling on each Si site with LS-coupling constant $\lambda_{\rm Si}$ which is experimentally determined as $\lambda_{\rm Si} = 29$ meV[13]. Here, the spin-orbit matrix $\boldsymbol{M}$ is

$$\boldsymbol{M} = \frac{1}{2} \begin{array}{c} \\ \langle p_x \uparrow | \\ \langle p_y \uparrow | \\ \langle p_z \uparrow | \\ \langle p_x \downarrow | \\ \langle p_y \downarrow | \\ \langle p_z \downarrow | \end{array} \begin{array}{c} \begin{array}{cccccc} |p_x \uparrow\rangle & |p_y \uparrow\rangle & |p_z \uparrow\rangle & |p_x \downarrow\rangle & |p_y \downarrow\rangle & |p_z \downarrow\rangle \end{array} \\ \begin{pmatrix} 0 & -i & 0 & 0 & 0 & 1 \\ i & 0 & 0 & 0 & 0 & -i \\ 0 & 0 & 0 & -1 & i & 0 \\ 0 & 0 & -1 & 0 & i & 0 \\ 0 & 0 & -i & -i & 0 & 0 \\ 1 & i & 0 & 0 & 0 & 0 \end{pmatrix} \end{array}. \tag{4}$$

The vacancy potential $H_{\rm vc}$ excludes electrons from the vacancy site by raising the energy levels Δ for the orbitals belong to the vacancy site. For $\Delta \longrightarrow \infty$, no electron exists at the vacancy site and then an effective vacancy state is realized.

In the absence of the vacancy ($\Delta = 0$), the Green's function for the perfect crystal is described as

$$G_{ij}^{0\alpha\beta}(z) = \sum_{\mathbf{k}s} \frac{u_{\alpha s}(\mathbf{k}) u_{\beta s}^{*}(\mathbf{k})}{z - \epsilon_{\mathbf{k}s}} e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)} \tag{5}$$

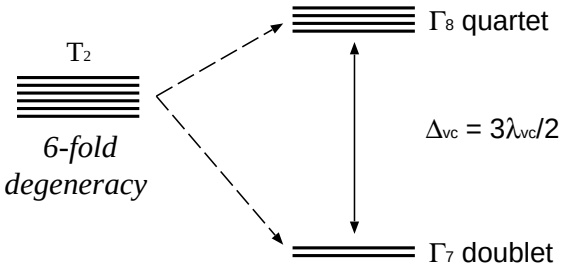

Figure 1. Spin-orbit splitting in the vacancy state $\Delta_{\rm vc}$ for the case with a positive value of the spin-orbit coupling on the vacancy state $\lambda_{\rm vc} > 0$.

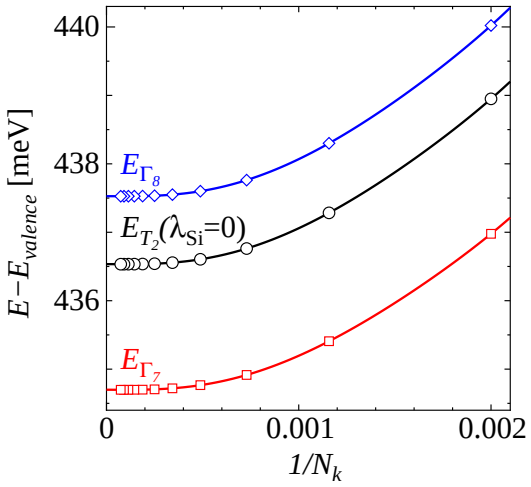

Figure 2. Vacancy levels E_{Γ_8} ($\diamondsuit$) and E_{Γ_7} ($\square$) for $\lambda_{\rm Si} = 43$ meV together with E_{T_2} ($\bigcirc$) for $\lambda_{\rm Si} = 0$ as functions of the inverse of total number of $\mathbf{k}$-points $1/N_k$.

where $u_{\alpha s}(\mathbf{k})$ is the eigenvector for the energy band $\epsilon_{\mathbf{k}s}$ given in eq. (2) and orbital m with spin σ, $\alpha = (m, \sigma)$. In the presence of the vacancy ($\Delta \neq 0$), the Green's function is obtained by solving the Dyson's equations which can be written in the 8×8 matrix representation as $\mathbf{G}_{ij} = \mathbf{G}^0_{ij} + \mathbf{G}^0_{i0}\mathbf{\Delta}\mathbf{G}_{0j}$, with the vacancy potential matrix $(\mathbf{\Delta})_{\alpha\beta} = \Delta\delta_{\alpha\beta}$, where $(\mathbf{G}^0_{ij})_{\alpha\beta} = G^{0\alpha\beta}_{ij}$ is the Green's function for $\Delta = 0$ given in eq. (5) and $(\mathbf{G}_{ij})_{\alpha\beta} = G^{\alpha\beta}_{ij}$ is the corresponding Green's function for $\Delta \neq 0$. In the limit $\Delta \to \infty$, $\mathbf{G}_{ij} \to 0$ with $i = 0$ and/or $j = 0$, and then $\mathbf{G}^0_{0j} + \mathbf{G}^0_{00}\mathbf{\Delta}\mathbf{G}_{0j} \to 0$. By using this relation, $\mathbf{G}_{ij}$ is obtained by $\mathbf{G}^0$ as $\mathbf{G}_{ij} = \mathbf{G}^0_{ij} - \mathbf{G}^0_{i0}\left(\mathbf{G}^0_{00}\right)^{-1}\mathbf{G}^0_{0j}$.

3. Results

We calculate $G^{0\alpha\beta}_{ij}$ in eq. (5) by performing the $\mathbf{k}$ summation with up to $20 \times 20 \times 10 = 4000$ mesh points and obtain $\mathbf{G}_{ij}$. When $\lambda_{\rm Si} = 0$, a remarkable localized level is found in the band gap and the total weight of this state is found to be 6 by summing the contribution to this level from all sites. Therefore, we find that this level corresponds to the T_2 states with the 6-fold spin-orbital degeneracy with the energy E_{T_2}. This localized level is occupied by two electrons in the V^0 state and by one electron in the V^+ state, respectively.

By introducing the LS coupling on each Si atom ($\lambda_{\rm Si} = 29$ meV), the T_2 states split into Γ_7 doublet groundstates and Γ_8 quartet excited states with a spin-orbit splitting on the vacancy states $\Delta_{\rm vc} > 0$ as shown in Fig.1. In Fig.2, the energy levels for the vacancy states, E_{T_2}, E_{Γ_8} and E_{Γ_7} measured relative to the valence band top, are plotted as functions of the inverse of total number of k-points $1/N_k$. Then, we obtain a $N_k \to \infty$ extrapolated value of the spin-orbit splitting on the vacancy states as $\Delta_{\rm vc} = 2.83$ meV which is of order of 1/10 of the spin-orbit splitting on Si atom $\Delta_{\rm Si} = 43$ meV[13]. Therefore, the spin-orbit coupling on the vacancy states $\lambda_{\rm vc}$ becomes extremely small as compared to $\lambda_{\rm Si}$ but is positive only due to the effect of spatial extension of the vacancy state.

Finally, we consider the effect of couplings between electrons and nonadiabatic Jahn-Teller phonons in the dangling bonds by using the Hamiltonian previously studied in Ref [7], which is an extention of the early Schlüter's model [5]. Within the second order perturbation theory,

we find that the groundstate becomes Γ_8 quartet for a realistic value of the electron-phonon coupling constant. The explicit results will be shown in a subsequent paper[14].

4. Summary and Discussion

In summary, we have investigated the electronic state around a single vacancy in infinite Si crystal on the basis of the Green's function approach. When the LS coupling $\lambda_{\rm Si}$ on each Si atom is taken into account, the T_2 states with the 6-fold spin-orbital degeneracy for the V^+ state split into Γ_7 doublet groundstates and Γ_8 quartet excited states with a reduced splitting energy of $O(\Delta_{\rm Si}/10)$. We have also considered the effect of couplings between electrons and Jahn-Teller phonons in the dangling bonds within the second order perturbation and find that the groundstate becomes Γ_8 quartet which is responsible for the magnetic-field suppression of the softening in B-doped Si.

In the present study, we have assumed that the T_d-point symmetry is preserved in a single vacancy in infinite Si crystal. Even in this case, the lattice relaxation with keeping the T_d-point symmetry might take place. Therefore, we have also investigated the effect of symmetry preserving lattice relaxation on the spin-orbit splitting in the vacancy states $\Delta_{\rm vc}$ by using the first-principle calculation with supercell method, and have found that $\Delta_{\rm vc}$ is positive in a single vacancy with an unitcell with 63 Si atoms [14]. To be more conclusive, we need further investigation to determine the explicit value of $\Delta_{\rm vc}$ with a larger size of supercell.

The effect of the electron correlation, which is considered to be important to determine the many-body groundstate in a Si vacancy as discussed from the cluster model calculations [6, 7, 8], has not been considered in this paper. The effect can be discussed by including the selfenergy corrections on the basis of the present Green's function approach and will be discussed in near future.

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